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**(54) Thermal barrier coating system**

## Wärmehemmendes Beschichtungssystem

### Revêtement de barrière thermique

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## Description

## FIELD OF THE INVENTION

5 [0001] The present invention relates to thermal barrier coating systems for nickel-based and cobalt-based superalloys.

## BACKGROUND OF THE INVENTION

10 [0002] Thermal barrier coating systems of various types are well known in the gas turbine engine industry as one means for protecting nickel-based and cobalt-based superalloy components, such as turbine blades and vanes, from oxidation and corrosion during engine operation.

[0003] One type of thermal barrier coating system involves depositing on the superalloy component (substrate) to be protected an MCrAlY metal alloy overlay where M is iron, nickel, cobalt, or a combination thereof, oxidizing the metal alloy overlay to form an alumina layer in-situ on the bondcoat, and then depositing a ceramic thermal barrier layer having columnar morphology on the alumina layer. Such a thermal barrier coating is described in U.S. Patents 4 321 310 and 4 321 311.

[0004] Another type of thermal barrier coating system exemplified by U.S. Patent 5 238 752 involves forming on the superalloy component (substrate) to be protected a high aluminum, atomically ordered intermetallic compound as a bondcoat. The intermetallic compound comprises, for example, equiatomic nickel aluminide (NiAl) having an Al content of 31.5 % by weight or platinum modified nickel aluminide known commercially as Chromaloy RT-22 having a high aluminum intermetallic NiAl Al matrix and including PtAl<sub>2</sub> phases in the coating microstructure. The intermetallic compound bondcoat is oxidized to form a thermally grown alumina layer in-situ thereon, and then a ceramic thermal barrier layer having columnar or other morphology is deposited on the alumina layer.

[0005] Still another type of thermal barrier coating system exemplified by U.S. Patents 4 880 614 and 5 015 502 involves forming on the superalloy component (substrate) to be protected a metallic bondcoat which may comprise an MCrAlY metal alloy overlay or a diffusion aluminide layer predominantly composed of aluminum intermetallic (e.g. NiAl, CoAl, and (Ni/Co)Al phases) which may be modified with Pt, Si, Hf, Cr, Mn, Ni, Co, Rh, Ta, Nb, and/or particulates, chemical vapor depositing (CVD) a high purity alpha alumina layer on the metallic bondcoat, and depositing a ceramic thermal barrier layer on the CVD alpha alumina layer.

[0006] In the manufacture of thermal barrier coating systems, the ceramic thermal barrier material, such as yttria stabilized zirconia, has been applied to the bondcoat by plasma spraying wherein coating adherence is promoted by the roughness of the bondcoat. Controlled porosity and microcracking within the ceramic thermal barrier layer accommodates strain developed due to the differences in thermal expansion coefficients between the ceramic and the substrate superalloy. Alternately, ceramic thermal barrier material has been applied to the bondcoat by physical vapor deposition (PVD), such as sputtering and electron beam evaporation, under conditions to produce a columnar morphology (i.e. independent ceramic columns) in the ceramic thermal barrier layer. This columnar morphology organizes the coating porosity between the columns to accommodate strain from thermal expansion mismatch between the substrate and ceramic thermal barrier layer.

[0007] An object of the present invention is to provide an improved thermal barrier coating system for use on gas turbine engine and other superalloy components or articles operating at elevated temperatures where oxidation and corrosion protection is needed.

[0008] Another object of the present invention is to provide a thermal barrier coating system by an improved method which results in advantages in the manufacture of thermal barrier coating systems.

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## SUMMARY OF THE INVENTION

[0009] The present invention provides a thermal barrier protected nickel based or cobalt based superalloy component, and method of making same, for use in a gas turbine engine wherein the thermal barrier coating system includes a multi-layered structure. The first bondcoat layer of the thermal barrier coating system comprises a chemical vapor deposited, platinum modified diffusion aluminide layer on the superalloy component (substrate). The diffusion aluminide layer includes an inner diffusion zone proximate the substrate and an outer layer region comprising a platinum modified (platinum-bearing) intermediate phase of aluminum and at least one of nickel and cobalt depending on the superalloy composition.

[0010] For example, for nickel based superalloy substrates, the intermediate nickel-aluminum phase resides in the beta solid solution intermediate phase region of the binary nickel-aluminum phase diagram. For cobalt based superalloy substrates, the intermediate phase resides in the zeta phase region of the binary cobalt-aluminum phase diagram. The intermediate phase is a solid solution having a range of compositions and is substantially free of other phase constit-

uents. The intermediate phase has an average aluminum concentration (through the outer layer region thickness) in the range of about 18 to about 28 % by weight, an average platinum concentration (through the layer thickness) in the range of about 8 to about 35% by weight, and an average nickel concentration (through the layer thickness) in the range of about 50 to 60% by weight and is non-stoichiometric relative to intermetallic compounds of aluminum and nickel, aluminum and cobalt, or aluminum and platinum. For example, the intermediate phase is hypostoichiometric in aluminum relative to the intermetallic compounds  $AlNi$  and  $Al_2Ni_3$  employed heretofore as bondcoats in thermal barrier coating systems.

[0011] The platinum modified diffusion aluminide layer preferably is formed by depositing a layer of platinum or alloy thereof on the substrate and chemical vapor depositing aluminum on the platinum covered substrate under high temperature and low aluminum activity conditions to form the inner diffusion zone and the outer intermediate phase region.

[0012] An adherent alumina layer is thermally grown on the diffusion aluminide layer by, for example, oxidizing the outer layer region in a low partial pressure oxygen atmosphere at a temperature greater than about 982.2°C (1800°F) that promote in-situ formation of alpha alumina. The thermally grown alumina layer receives an outer ceramic thermal barrier layer thereon, preferably deposited by electron beam evaporation of ceramic thermal barrier material and condensation on the alumina layer.

[0013] The invention is advantageous in that a kinetically stable diffusion aluminide layer is produced by a long time CVD exposure at high temperature/low aluminum activity to produce a diffusion aluminide layer with an intermediate, non-stoichiometric single phase microstructure formed at the outer layer region on top of which the alumina layers and ceramic thermal barrier layer reside. The spallation of the ceramic thermal barrier layer is improved significantly as compared to thermal barrier spallation on a like substrate having a two-phase (stoichiometric  $NiAl$  plus  $PtAl_2$  intermetallic) platinum modified diffusion aluminide bondcoat (the aforementioned RT22 aluminide) with a thermally grown alumina layer between the bondcoat and the thermal barrier layer.

#### DESCRIPTION OF THE DRAWINGS

[0014] Figure 1 is a scanning electron micrograph of a thermal barrier protected nickel based substrate in accordance with an embodiment of the present invention.

[0015] Figure 2 is a phase diagram for the binary nickel-aluminum system.

[0016] Figure 3 is similar to Figure 1 but marked to indicate how chemical analyses were conducted for Al, Pt, and Ni in the bondcoat by microprobe using wavelength dispersive spectroscopy.

[0017] Figure 4 is a schematic diagram of ceramic thermal barrier coating apparatus that can be used in practicing the invention.

#### DESCRIPTION OF THE INVENTION

[0018] Figure 1 is a scanning electron micrograph of a thermal barrier protected nickel-based superalloy substrate in accordance with an embodiment of the present invention. As is apparent, the thermal barrier coating system comprises a multi-layered structure comprising a first bondcoat layer designated MDC-150L in Figure 1, a thermally grown alumina layer on the bondcoat, and a ceramic thermal barrier layer designated EB-TBC on the thermally grown alumina layer.

[0019] The present invention can be used with known nickel based and cobalt based superalloy substrates, which may comprise equiaxed, DS (directionally solidified) and SC (single crystal) castings as well as other forms of these superalloys, such as forgings, pressed superalloy powder components, machined components, and other forms. For example only, the examples set forth below employ the well-known Rene' alloy N5 nickel base superalloy having a composition of Ni-7.0% Cr- 6.2% Al-7.5% Co-6.5% Ta-1.5% Mo-5.0% W-3.0% Re-0.15% Hf-0.05% C-0.018% Y (all by weight) used for making SC turbine blades and vanes. Other nickel base superalloys which can be used include, but are not limited to, MarM247, CMSX-4, PWA 1422, PWA 1480, PWA-1484, Rene' 80, Rene' 142, and SC 180. Cobalt based superalloys which can be used include, but are not limited to, FSX-414, X-40, and MarM509.

[0020] The bondcoat layer designated MDC-150L comprises a chemical vapor deposited, platinum modified diffusion aluminide layer on the Ni-based superalloy substrate. The diffusion aluminide layer includes an inner diffusion zone proximate the nickel base superalloy substrate, and an outer layer region comprising a platinum modified (platinum bearing) intermediate phase of aluminum and nickel (or cobalt, depending on the superalloy composition). The overall thickness of the bondcoat is in the range of about 38.1 to about 76.2 micrometers (1.5 to 3.0 mils).

[0021] For example, for nickel based superalloy substrates, the intermediate nickel-aluminum phase resides in the beta solid solution intermediate phase region of the binary nickel-aluminum phase diagram shown in Figure 2. For cobalt based superalloy substrates, the intermediate phase resides in the zeta phase region of the binary cobalt-aluminum phase diagram which can be found in Binary Alloy Phase Diagrams, American Society of Metals, Editor-In-Chief Thaddeus B. Massalski, 1986. The intermediate phase is a metallic solid solution having a range of compositions

and is substantially free of other phase constituents (i.e. minor amounts such as less than 5 volume % of other phases may occur in the microstructure).

[0022] The intermediate phase has an average aluminum concentration (through the layer thickness) in the range of about 18 to about 28 % by weight, an average platinum concentration (through the layer thickness) in the range of about 8 to about 35% by weight, and an average nickel concentration (through the layer thickness) in the range of about 50 to 60% by weight and is non-stoichiometric relative to intermetallic compounds of aluminum and nickel, aluminum and cobalt, and aluminum and platinum. For example, the intermediate phase is hypostoichiometric in aluminum relative to the intermetallic compounds  $AlNi$  and  $Al_2Ni_3$  employed heretofore as bondcoats in thermal barrier coating systems.

[0023] When the substrate is first platinum plated followed by CVD aluminizing, the aluminum and platinum concentrations in the intermediate phase layer are graded such that the aluminum concentration is highest at an outer surface of the outer layer region and the platinum concentration is highest proximate the inner diffusion zone. The nickel concentration decreases from the outer surface toward the diffusion zone.

[0024] The platinum modified diffusion aluminide layer preferably is formed by depositing a layer of platinum or alloy thereof on the substrate and chemical vapor depositing aluminum on the platinum covered substrate under high temperature and low aluminum activity conditions described in US 5,658,614 to which reference is hereby made with respect to CVD formation of the platinum modified diffusion aluminide layer. The deposition conditions are controlled to form the inner diffusion zone Z of Figure 1 and the outer intermediate single phase region P of Figure 1 as an additive region to the nickel based superalloy substrate by virtue of outward diffusion of substrate nickel and other substrate alloying elements. Other elements may be added to the bondcoat during CVD formation, for example, such elements as Si, Hf, Y, and other Lanthanide and Actinide series elements with favorable chlorination thermodynamics can be added to the layer as disclosed in the aforementioned US 5,658,614.

[0025] For example, generally, the substrate is electroplated with a 9-11 milligram/centimeter squared platinum layer (e.g. 50.8 micrometers (2 mil) thick Pt layer) and then subjected, without a Pt prediffusion treatment, to CVD aluminizing at a substrate temperature greater than 1000 °C (e.g. 1080 °C) and contacting a high purity coating gas mixture comprising hydrogen carrier gas (less than 30 parts per billion impurities) and aluminum trichloride gas (less than 25 parts per million impurities) that result in a decrease in the concentrations of deleterious substrate substitutional alloying elements, such as W, Cr, Ti, and Mo, and surface active tramp elements, such as B, P, and S.

[0026] A typical CVD coating gas mixture comprises 9 volume % aluminum trichloride and 91 volume % hydrogen at a flow rate of 8,495 m<sup>3</sup>/min (300 scfm). More generally, the aluminum trichloride gas typically does not exceed 10 volume % of the coating gas mixture, and preferably is in the range of 4 to 6 volume % of the coating gas mixture. The coating gas flow rate typically is within the range of 5,663 to 11,327 m<sup>3</sup>/min (200 to 400 scfm). As mentioned, the substrate temperature is greater than 1000 °C.

[0027] Coating gas mixture for forming the bondcoat can be generated by passing high purity hydrogen (less than 30 ppb impurities) and high purity hydrogen chloride (less than 25 ppm impurities) in mixture of hydrogen/13 volume % HCl over a 99.999% pure source of aluminum at 290 °C as set forth in the aforementioned US 5,658,614.

[0028] The thin adherent alpha alumina layer is thermally grown on the diffusion aluminide layer designated MDC-150L under conditions effective to form an alpha alumina layer, rather than other forms of alumina, such as gamma alumina. For example, the diffusion aluminide layer is oxidized in a low partial pressure oxygen atmosphere, such as a vacuum less than  $10^{-4}$  torr, or argon or hydrogen partial pressures having oxygen impurities at temperatures greater than about 982.2°C (1800°F) that promote in-situ formation of the alpha phase alumina. The thickness of the alpha alumina layer is in the range of about 0.01 to 2 micrometers.

[0029] For purposes of illustration, the alpha alumina layer can be formed in-situ by evacuating a vacuum furnace to  $1 \times 10^{-6}$  torr and backfilling with argon having oxygen impurities to 10 torr, ramping the substrate having the platinum modified diffusion aluminide layer thereon to 1051.7°C (1925°F) holding at temperature for one hour, and cooling to room temperature for removal from the furnace.

[0030] The thermally grown alpha alumina layer receives an outer ceramic thermal barrier layer designated EB-TBC in Figure 1. In one embodiment of the invention, the ceramic thermal barrier layer can be deposited on the alpha alumina layer by electron beam physical vapor deposition apparatus shown schematically in Figure 4 wherein a source (e.g. ingot feeder in Figure 1) of ceramic thermal barrier material is evaporated by electron beam heating from the electron beam gun and condensed on the alpha alumina layer of the substrate(s) S positioned and rotated in a coating chamber typically above the source of ceramic thermal barrier material in the vapor cloud from the source.

[0031] For example, the loading and preheat chamber shown connected to the thermal barrier coating chamber is first evacuated to below  $1 \times 10^{-4}$  torr and the substrate mounted on a rotatable shaft (part manipulator) is heated therein to 954.4°C (1750°F) in the loading/preheat chamber. In the coating chamber, an electron beam (power level of 65 kW) from the electron beam gun is scanned (rate of 750 Hertz) over an ingot I of yttria stabilized zirconia (or other thermal barrier ceramic material) to evaporate it. The electron beam scans the ingot at an angle to avoid the substrate and back reflection of the beam. For zirconia based materials, oxygen is introduced into the coating chamber to produce

5 a pressure of 1-20 micrometers ensuring a deposition of a white near-stoichiometric yttria stabilized zirconia deposit is formed on the alumina. To minimize heat loss, the preheated coated substrate(s) S then is/are rapidly moved on the shaft from the loading/preheat chamber to a coating position in heat reflective enclosure E in the coating chamber above the ingot I. The enclosure includes an opening for the electron beam to enter. The substrate is rotated by the shaft at a speed of 30 rpm about 27.94 cm (11 inches) above the ingot, although the spacing can be from about 25.4-38.1 cm (11-15 inches). Deposition is conducted for a time to produce the desired thickness of ceramic thermal barrier layer. Typical thickness of the thermal barrier layer is in the range of 101.6 to 304.8 micrometers (4 to 12 mils or 0.004 to 0.012 inch).

10 [0032] The present invention is not limited to forming a thermal barrier layer having columnar grain microstructure shown in Figure 1. Other thermal barrier layer structures may be employed. For example, a plurality of alternating thin layers of yttria stabilized zirconia and alumina (each approximately one micrometer thick) can be electron beam PVD deposited on the alumina layer as the thermal barrier layer. The number of individual ceramic layers can be controlled to provide a desired thermal barrier layer thickness.

15 [0033] For purposes of illustration and not limitation, substrate specimens of a thermal barrier protected Rene' alloy N5 substrate were made pursuant to an embodiment of the invention for cyclic oxidation testing. The specimens were 25.4 mm (one inch) in diameter and 3.175 mm (0.125 inches) in thickness and were ground flat and then media finished with polishing stones to round sharp edges. The bondcoat designated MDC-150L was formed using the following parameters:

20 substrate temperature: 1079.4 °C (1975 °F)

coating gas: 7,9287 m<sup>3</sup> per hour (280 cubic feet per hour) hydrogen and 0.34 m<sup>3</sup> per hour (12 cubic feet per hour) of HCl to generate AlCl<sub>3</sub> from the aforementioned high purity aluminum bed

25 coating gas flow rate: 8.268 m<sup>3</sup> per hour (292 cubic feet per hour)

for a coating time to yield an MDC-150L coating thickness of 61 to 66 micrometers (2.4 to 2.6 mils) on the substrate specimens.

30 [0034] The alpha alumina layer was formed on the bondcoat coated specimens by heat treating in an argon environment by first evacuating a vacuum chamber to  $1.33 \times 10^{-4}$  Pa ( $1 \times 10^{-6}$  torr) and backfilling to  $1.33 \times 10^3$  Pa (10 torr) with shop argon having sufficient oxygen impurities to form alumina at temperature, ramping the substrate to temperature of above  $982.2^\circ\text{C} = 1800^\circ\text{F}$  (e.g.  $1051.67^\circ\text{C} = 1925^\circ\text{F}$ ), holding at temperature for one hour, and cooling to room temperature for removal from the furnace.

35 [0035] Eight substrate specimens next were attached on the rotatable shaft of the aforementioned electron beam PVD coating apparatus in the loading/preheat chamber. The chamber was evacuated  $10^{-4}$  torr and the substrate specimens heated to  $960^\circ\text{C}$  ( $1760^\circ\text{F}$ ). Once the specimen temperature had equilibrated, the specimens were translated on the shaft into the coating chamber. Prior to movement into the coating chamber, the coating chamber was stabilized to achieve an oxygen pressure of 6-8 micrometers at  $1077^\circ\text{C}$  ( $1970^\circ\text{F}$ ) while the electron beam at a power level of 65 kW was scanned at a rate of 750 Hertz across a 7-8 weight % yttria stabilized zirconia ingot. The specimens were rotated at 30 rpm over the molten ceramic pool in the vapor cloud for 19 minutes to deposit a 106.7 to 111.8 micrometers (4.2 to 4.4 mil) thick columnar yttria stabilized zirconia coating on the alpha alumina layer.

40 [0036] A typical microstructure of the thermal barrier coating system so formed is shown in Figure 1 and described hereabove. As is apparent, the thermal barrier coating system comprises a multi-layered structure comprising the first bondcoat layer designated MDC-150L, the thermally grown alumina layer on the bondcoat, and the ceramic thermal barrier layer designated EB-TBC on the thermally grown alumina layer.

45 [0037] Table I below sets forth Al, Pt, and Ni average concentrations through the thickness of the bondcoat for several alloy N5 substrate specimens with the thermal barrier layer.

50 [0038] The alloyant concentrations were measured by a microprobe using wavelength dispersive spectroscopy wherein an electron beam is controlled to form a box pattern or shape approximately 5 micrometers by 5 micrometers in dimension from which X-rays characteristic of the elements present are emitted and analyzed. A line of usually 5 such analysis boxes was used to make measurements from the top of the bondcoat progressively toward the diffusion zone Z through the bondcoat thickness (e.g. see Figure 3).

55 [0039] The data for each of Al, Pt, and Ni from each analysis box were averaged for each line. This measuring technique was repeated at five different locations (at five different electron beam lines) on the bondcoat. The averaged data for each different line or location #1-5 is set forth in Table I along with the average data for all lines and all data.

TABLE I

5	Mount No.	Alloy	Run No.	TBC				Average Wt. %
				Al	Pt	Ni	Others	
10	71288	N5	1-27	21.5	15.6	54.1	8.8	# 1
				21.3	15.6	54.6	8.5	# 2
				21.6	15.9	55.1	7.4	# 3
				21.5	16.4	54.1	8.0	# 4
				21.4	16.6	54.8	7.2	# 5
				Average	21.5	16.0	54.6	8.0
15	71285	N5	1-27	Minimum	19.9	14.0	52.1	
				Maximum	22.8	17.6	57.3	
				22.1	15.5	53.4	9.0	# 1
				22.5	15.8	54.5	7.2	# 2
				22.7	16.0	54.6	7.5	# 3
				22.2	16.2	53.6	8.0	# 4
20	71284	N5	1-27	22.5	15.8	54.0	7.7	# 5
				Average	22.4	15.9	54.0	7.7
				Minimum	20.9	13.3	51.9	
				Maximum	24.2	17.4	57.4	
				23.0	15.4	54.5	7.1	# 1
				22.4	16.6	53.5	7.5	# 2
25	71284	N5	1-27	22.6	16.4	54.0	7.0	# 3
				22.5	16.7	53.8	7.0	# 4
				22.3	17.7	53.2	8.8	# 5
				Average	22.6	16.8	53.8	7.0
				Minimum	20.5	11.9	51.1	
				Maximum	25.3	19.3	58.6	
30	71284	N5	1-27	All Data				
				Average Wt. %				
				Al	Pt	Ni	Others	
				Average	22.2	16.2	54.1	
				Minimum	19.9	11.9	51.1	
				Maximum	25.3	19.3	58.6	
35	71284	N5	1-27	All Data				
				Average Wt. %				
				Al	Pt	Ni	Others	
				Average	22.6	16.8	53.8	
				Minimum	20.5	11.9	51.1	
				Maximum	25.3	19.3	58.6	
40	71284	N5	1-27	All Data				
				Average Wt. %				
				Al	Pt	Ni	Others	
				Average	22.2	16.2	54.1	
				Minimum	19.9	11.9	51.1	
				Maximum	25.3	19.3	58.6	

[0040] The specimens were tested in a 1135°C (2075°F) cyclic oxidation test where the thermal barrier protected specimens of the invention were subjected to test cycles each 60 minutes in duration consisting of a 1135°C (2075°F) exposure for 50 minutes in air followed by 10 minutes of cooling in air to below 149°C (300°F). The following Table II summarizes the cyclic oxidation testing. For comparison, thermal barrier spallation on a like Alloy N5 substrate having a two-phase (stoichiometric NiAl plus PtAl<sub>2</sub> intermetallic) platinum modified diffusion aluminide bondcoat (the aforementioned RT22 aluminide) with a thermally grown alumina layer between the bondcoat and the thermal barrier layer is shown in Table II.

TABLE II

Ceramic Spallation Test			
Bondcoat	Tests	Ave. Cycles to Failure	
MDC-150L	3	820	
Prior Art (Platinum Aluminide)	10	380	

[0041] It is apparent that the thermal barrier coating system of the specimens of the invention exhibited spallation of the yttria stabilized zirconia layer after an average of 820 cycles as compared to only 380 cycles to spallation for the comparsion specimens outside the invention.

[0042] The invention is advantageous in that a thermally stable diffusion aluminide layer is produced by high temperature/low aluminum activity/relatively long time CVD exposure to produce an outward diffusion aluminide layer with an intermediate, non-stoichiometric single phase microstructure formed at the outer layer region on top of which the alumina layer and ceramic thermal barrier layer reside.

[0043] As it becomes obvious from the foregoing description, preferred embodiments of the inventive article have a thermally grown alpha alumina layer on the aluminide layer.

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### Claims

1. An article for use in a gas turbine engine, comprising:

a substrate comprising at least one of a nickel based superalloy and cobalt based superalloy, a chemical vapor deposited, diffusion aluminide layer formed on the substrate, said aluminide layer having an outer layer region comprising a solid solution intermediate phase and having an inner diffusion zone region proximate the substrate, said intermediate phase having an average aluminum concentration in the range of about 18 to about 28% by weight, an average platinum concentration in the range of about 8 to about 35% by weight, and an average nickel concentration in the range of about 50 to about 60% by weight so as to be non-stoichiometric relative to intermetallic compounds of aluminum and nickel, aluminum and cobalt, or aluminum and platinum, said outer layer region being substantially free of phase constituents other than said intermediate phase, an alumina layer on the aluminide layer, and a ceramic thermal barrier layer on the alumina layer.

2. The article of claim 1, wherein the substrate is a nickel based superalloy and said intermediate phase resides in the beta solid solution-intermediate phase region of the binary nickel-aluminum phase diagram.

3. The article of claim 1, wherein the substrate is a cobalt based superalloy and said intermediate phase resides in the zeta phase region of the binary cobalt-aluminum phase diagram.

4. The article of claim 1, wherein said outer layer region is about 2.54 to 76.2 micrometers (0.1 to 3.0 mils) in thickness.

5. The article of claim 1, wherein said ceramic thermal barrier layer comprises a columnar microstructure.

6. The article of claim 1, wherein said ceramic thermal barrier layer comprises alternating layers of ceramic thermal barrier material.

7. The article of claim 1, wherein the ceramic thermal barrier layer comprises yttria stabilized zirconia.

8. The article of claim 1, wherein the aluminum concentration of said intermediate phase is highest at an outer surface of said outer layer region and said platinum concentration of said intermediate phase is highest proximate the diffusion zone.

9. An article for use in a gas turbine engine, comprising:

a nickel base superalloy substrate, a chemical vapor deposited, diffusion aluminide layer formed on the substrate, said aluminide layer having an outer layer region comprising a nickel-aluminum solid solution intermediate beta phase and an inner diffusion zone region proximate the substrate, said intermediate phase having an average aluminum concentration in the range of about 18 to about 28% by weight, an average platinum concentration in the range of about 8 to about 35% by weight, and an average nickel concentration in the range of about 50 to about 60% by weight so as to be non-stoichiometric relative to intermetallic compounds of aluminum and nickel and of aluminum and platinum, said outer layer region being free of phase constituents other than said intermediate beta phase, a thermally grown alpha alumina layer on the aluminide layer, and a ceramic thermal barrier layer vapor deposited on the alumina layer to have a columnar microstructure.

10. The article of claim 7, wherein said outer layer region is about 2.54 to 76.2 micrometers (0.1 to 3.0 mils) in thickness.

11. The article of claim 7, wherein the ceramic thermal barrier layer comprises yttria stabilized zirconia.

12. A method of forming a thermal barrier coating on a substrate that comprises at least one of nickel based superalloy and cobalt based superalloy, comprising:

depositing a layer of platinum or alloy thereof on the substrate and chemical vapor depositing aluminum on the platinum covered substrate under high temperature and low aluminum activity conditions, such that a diffusion aluminide layer is formed on the substrate that provides an outer aluminide layer region comprising a solid solution intermediate phase and an inner diffusion zone region proximate the substrate, wherein said intermediate phase has an average aluminum concentration in the range of about 18 to about 28% by weight, an average platinum concentration in the range of about 8 to about 35% by weight, and an average nickel concentration of about 50 to about 60% by weight so as to be non-stoichiometric relative to intermetallic compounds of aluminum and nickel, aluminum and cobalt or aluminum and platinum, said outer layer region being substantially free of phase constituents other than said intermediate phase, oxidizing the aluminide layer under temperature and oxygen partial pressure conditions effective to form an alpha alumina layer, and depositing a ceramic thermal barrier layer on the alumina layer.

13. The method of claim 12, wherein the substrate is a nickel-based superalloy and said intermediate phase resides in the beta solid solution intermediate phase region of the binary nickel-aluminum phase diagram.

14. The method of claim 12, wherein the substrate is a cobalt-based superalloy and said intermediate phase resides in the zeta phase region of the binary cobalt-aluminum phase diagram.

15. The method of claim 12, wherein said outer layer region is formed to a thickness of about 2.54 to 76.2 micrometers (0.1 to 3.0 mils).

16. The method of claim 12, wherein said alumina layer is formed by heating the diffusion aluminide layer at a temperature greater than 982.2 degrees C (1800 degrees F) at a partial pressure of oxygen less than  $1.33 \cdot 10^{-4}$  Pa ( $10^{-6}$  torr).

17. Method of claim 12, wherein said ceramic thermal barrier layer is deposited by vapor condensation on said substrate so as to have a columnar microstructure.

### Patentansprüche

1. Gegenstand zur Verwendung in einer Gasturbine, umfassend:

ein Substrat aus mindestens einer auf Nickel und/oder Cobalt basierenden Superlegierung, eine durch chemisches Aufdampfen auf dem Substrat gebildete Diffusionsaluminidschicht, wobei die Aluminidschicht einen äußeren Schichtbereich mit einer als feste Lösung vorliegenden Zwischenphase und einen nächst dem Substrat gelegenen inneren Diffusionszonenbereich hat, wobei die Zwischenphase eine durchschnittliche Aluminiumkonzentration im Bereich von etwa 18 bis etwa 28 Gew.-%, eine durchschnittliche Platin-Konzentration im Bereich von etwa 8 bis etwa 35 Gew.-% und eine durchschnittliche Nickelkonzentration im Bereich von etwa 50 bis etwa 60 Gew.-% aufweist, sodaß sie bezüglich der intermetallischen Verbindungen von Aluminium und Nickel, Aluminium und Cobalt oder Aluminium und Platin nichtstöchiometrisch ist, wobei der äußere Schichtbereich im wesentlichen frei von anderen Phasenbestandteilen als der Zwischenphase ist, eine Aluminiumoxidschicht auf der Aluminidschicht und eine keramische Wärmedämmsschicht auf der Aluminiumoxidschicht.

2. Gegenstand nach Anspruch 1, worin das Substrat eine Superlegierung auf Nickelbasis ist und die Zwischenphase im binären Nickel-Aluminium-Phasendiagramm im Bereich der als feste Lösung vorliegenden beta-Zwischenphase liegt.

3. Gegenstand nach Anspruch 1, worin das Substrat eine Superlegierung auf Cobaltbasis ist und die Zwischenphase im zeta-Phasenbereich des binären Cobalt-Aluminium-Phasendiagramms liegt.

4. Gegenstand nach Anspruch 1, worin der äußere Schichtbereich etwa 2,54 bis 76,2 Mikrometer (0,1 bis 3,0 mils) dick ist.
5. Gegenstand nach Anspruch 1, worin die keramische Wärmedämmsschicht eine säulenförmige Mikrostruktur aufweist.
6. Gegenstand nach Anspruch 1, worin die keramische Wärmedämmsschicht abwechselnde Schichten von keramischem Wärmedämmmaterial aufweist.
10. 7. Gegenstand nach Anspruch 1, worin die keramische Wärmedämmsschicht Yttriumoxid-stabilisiertes Zirkoniumdioxid aufweist.
15. 8. Gegenstand nach Anspruch 1, worin die Aluminiumkonzentration der Zwischenphase an der Außenfläche des äußeren Schichtbereichs am höchsten ist und die Platinkonzentration der Zwischenphase nächst der Diffusionszone am höchsten ist.
9. Gegenstand zur Verwendung in einer Gasturbine, umfassend:
  20. ein Substrat aus einer Superlegierung auf Nickelbasis, eine durch chemisches Aufdampfen auf dem Substrat gebildete Diffusionsaluminidschicht, wobei die Aluminidschicht einen äußeren Schichtbereich mit einer als feste Lösung vorliegenden Nickel-Aluminium-beta-Zwischenphase und einen nächst dem Substrat gelegenen inneren Diffusionszonenbereich hat, wobei die Zwischenphase eine durchschnittliche Aluminiumkonzentration im Bereich von etwa 18 bis etwa 28 Gew.-%, eine durchschnittliche Platinkonzentration im Bereich von etwa 8 bis etwa 35 Gew.-% und eine durchschnittliche Nickelkonzentration im Bereich von etwa 50 bis etwa 60 Gew.-% aufweist, sodaß sie bezüglich der intermetallischen Verbindungen von Aluminium und Nickel und Aluminium und Platin nichtstöchiometrisch ist, wobei der äußere Schichtbereich frei von anderen Phasenbestandteilen als der beta-Zwischenphase ist, eine thermisch gewachsene alpha-AluminiumoxidSchicht auf der Aluminidschicht und eine keramische Wärmedämmsschicht, die auf die Aluminiumoxidschicht aufgedampft ist und eine säulenförmige Mikrostruktur aufweist.
  30. 10. Gegenstand nach Anspruch 9, worin der äußere Schichtbereich etwa 2,54 bis 76,2 Mikrometer (0,1 bis 3,0 mils) dick ist.
  35. 11. Gegenstand nach Anspruch 9, worin die keramische Wärmedämmsschicht Yttriumoxid-stabilisiertes Zirkoniumdioxid aufweist.
  40. 12. Verfahren zur Bildung einer Wärmedämmbeschichtung auf einem Substrat aus mindestens einer auf Nickel und/oder Cobalt basierenden Superlegierung, umfassend:
    45. Aufbringen einer Schicht Platin oder Platinlegierung auf das Substrat und chemisches Aufdampfen von Aluminium auf das mit Platin bedeckte Substrat unter Bedingungen hoher Temperatur und niedriger Aluminiumaktivität, sodaß auf dem Substrat eine Diffusionsaluminidschicht gebildet wird, welche einen äußeren Aluminid-Schichtbereich mit einer als feste Lösung vorliegenden Zwischenphase und einen nächst dem Substrat gelegenen inneren Diffusionszonenbereich vorsieht, wobei die Zwischenphase eine durchschnittliche Aluminiumkonzentration im Bereich von etwa 18 bis etwa 28 Gew.-%, eine durchschnittliche Platinkonzentration im Bereich von etwa 8 bis etwa 35 Gew.-% und eine durchschnittliche Nickelkonzentration im Bereich von etwa 50 bis etwa 60 Gew.-% aufweist, sodaß sie bezüglich der intermetallischen Verbindungen von Aluminium und Nickel, Aluminium und Cobalt oder Aluminium und Platin nichtstöchiometrisch ist, wobei der äußere Schichtbereich im wesentlichen frei von anderen Phasenbestandteilen als der Zwischenphase ist, Oxidieren der Aluminidschicht unter Bedingungen der Temperatur und des Sauerstoff-Partialdrucks, die wirksam sind, um eine alpha-Aluminiumoxidschicht zu bilden, und 50. Aufbringen einer keramischen Wärmedämmsschicht auf die Aluminiumoxidschicht.
    55. 13. Verfahren nach Anspruch 12, worin das Substrat eine Superlegierung auf Nickelbasis ist und die Zwischenphase im binären Nickel-Aluminium-Phasendiagramm im Bereich der als feste Lösung vorliegenden beta-Zwischenphase liegt.

14. Verfahren nach Anspruch 12, worin das Substrat eine Superlegierung auf Cobaltbasis ist und die Zwischenphase im Bereich des zeta-Phasenbereichs des binären Cobalt-Aluminium-Phasendiagramms liegt.

5 15. Verfahren nach Anspruch 12, worin der äußere Schichtbereich eine Dicke von etwa 2,54 bis 76,2 Mikrometer (0,1 bis 3,0 mils) aufweist.

10 16. Verfahren nach Anspruch 12, worin die Aluminiumoxidschicht durch Erhitzen der Diffusionsaluminidschicht auf eine Temperatur von mehr als 982,2°C (1800°F) bei einem Sauerstoff-Partialdruck von weniger als  $1,33 \cdot 10^{-4}$  Pa ( $10^{-6}$  Torr) gebildet wird.

17. Verfahren nach Anspruch 12, worin die keramische Wärmedämmsschicht durch Dampfkondensation auf dem Substrat abgeschieden wird, sodaß sie eine säulenförmige Mikrostruktur aufweist.

## 15 Revendications

1. Article à utiliser dans un moteur à turbine à gaz, comprenant

20 un substrat comprenant au moins l'un parmi un superalliage à base de nickel et un superalliage à base de cobalt, une couche d'aluminure de diffusion déposée en phase vapeur par procédé chimique formée sur le substrat, ladite couche d'aluminure ayant une région de couche extérieure comprenant une phase intermédiaire en solution solide et ayant une région de zone de diffusion intérieure à proximité du substrat, ladite phase intermédiaire ayant une concentration moyenne d'aluminium située dans la plage allant d'environ 18 à environ 28 % en poids, une concentration moyenne de platine située dans la plage allant d'environ 8 à environ 35 % en poids, et une concentration moyenne de nickel située dans la plage allant d'environ 50 à environ 60 % en poids de façon à être non stoechiométrique en ce qui concerne les composés inter métalliques d'aluminium et nickel, d'aluminium et cobalt, ou d'aluminium et platine; ladite région de couche extérieure étant pratiquement exempte de constituants de phase autres que ladite phase intermédiaire,

30 une couche d'alumine sur la couche d'aluminure, et une couche de barrière thermique céramique déposée sur la couche d'alumine.

2. Article selon la revendication 1, dans lequel le substrat est un superalliage à base de nickel et ladite phase intermédiaire se trouve dans la région de phase intermédiaire en solution solide bêta du diagramme de phase binaire nickel/aluminium.

35 3. Article selon la revendication 1, dans lequel le substrat est un superalliage à base de cobalt et ladite phase intermédiaire se trouve dans la région de phase zéta du diagramme de phase binaire cobalt/aluminium.

40 4. Article selon la revendication 1, dans lequel ladite région de couche extérieure a une épaisseur d'environ 2,54 à 76,2 micromètres (0,1 à 3,0 mils).

5. Article selon la revendication 1, dans lequel ladite couche de barrière thermique céramique comprend une microstructure colonnnaire.

45 6. Article selon la revendication 1, dans lequel ladite couche de barrière thermique céramique comprend des couches en alternance de matériau de barrière thermique céramique.

7. Article selon la revendication 1, dans lequel la couche de barrière thermique céramique comprend de la zirconia stabilisée à lyttria.

50 8. Article selon la revendication 1, dans lequel la concentration d'aluminium de ladite phase intermédiaire est maximale au niveau d'une surface extérieure de ladite région de couche extérieure et ladite concentration de platine de ladite phase intermédiaire est maximale à proximité de la zone de diffusion.

55 9. Article à utiliser dans un moteur à turbine à gaz, comprenant

un substrat en superalliage à base de nickel,

une couche d'aluminure de diffusion déposée en phase vapeur par procédé chimique formée sur le substrat, ladite couche d'aluminure ayant une région de couche extérieure comprenant une phase bêta intermédiaire en solution solide nickel/aluminium et une région de zone de diffusion intérieure à proximité du substrat, ladite phase intermédiaire ayant une concentration moyenne d'aluminium située dans la plage allant d'environ 18 à environ 28 % en poids, une concentration moyenne de platine située dans la plage allant d'environ 8 à environ 35 % en poids, et une concentration moyenne de nickel située dans la plage allant d'environ 50 à environ 60 % en poids de façon à être non stoechiométrique en ce qui concerne les composés intermétalliques d'aluminium et nickel et d'aluminium et platine, ladite région de couche extérieure étant exempte de constituants de phase autres que ladite phase bêta intermédiaire,

une couche d' $\alpha$ -alumine ayant subi une croissance thermique sur la couche d'aluminure, et

une couche de barrière thermique céramique déposée par métallisation sous vide sur la couche d'alumine pour avoir une microstructure colonnaire.

10. Article selon la revendication 9, dans lequel ladite région de couche extérieure a une épaisseur d'environ 2,54 à 15 76,2 micromètres (0,1 à 0,3 mil).

11. Article selon la revendication 9, dans lequel la couche de barrière thermique céramique comprend de la zirconia stabilisée à l'yttria.

20. 12. Procédé pour former un revêtement de barrière thermique sur un substrat qui comprend au moins l'un parmi un superalliage à base de nickel et un superalliage à base de cobalt, comprenant

la déposition d'une couche de platine ou d'un alliage de celui-ci sur le substrat et la déposition en phase vapeur par procédé chimique d'aluminium sur le substrat recouvert de platine dans des conditions de température élevée et de faible activité d'aluminium, de telle sorte qu'une couche d'aluminure de diffusion soit formée sur le substrat, laquelle réalise une région de couche d'aluminure extérieure comprenant une phase intermédiaire en solution solide et une région de zone de diffusion intérieure proche du substrat, dans laquelle ladite phase intermédiaire a une concentration moyenne d'aluminium située dans la plage allant d'environ 18 à environ 28 % en poids, une concentration moyenne de platine située dans la plage allant d'environ 8 à environ 35 % en poids, et une concentration moyenne de nickel située dans la plage allant d'environ 50 à environ 60 % en poids de façon à être non stoechiométrique en ce qui concerne les composés intermétalliques d'aluminium et nickel, d'aluminium et cobalt ou d'aluminium et platine, ladite région de couche extérieure étant pratiquement exempte de constituants de phase autres que ladite phase intermédiaire,

l'oxydation de la couche d'aluminure dans des conditions de température et de pression partielle d'oxygène efficaces pour former une couche d' $\alpha$ -alumine, et

la déposition d'une couche de barrière thermique céramique sur la couche d'alumine.

35. 13. Procédé selon la revendication 12, dans lequel le substrat est un superalliage à base de nickel et ladite phase intermédiaire se trouve dans la région de phase intermédiaire en solution solide bêta du diagramme de phase binaire nickel/aluminium.

40. 14. Procédé selon la revendication 12, dans lequel le substrat est un superalliage à base de cobalt et ladite phase intermédiaire se trouve dans la région de phase zéta du diagramme de phase binaire cobalt/aluminium.

45. 15. Procédé selon la revendication 12, dans lequel ladite région de couche extérieure est formée en une épaisseur d'environ 2,54 à 76,2 micromètres (0,1 à 3,0 mils).

50. 16. Procédé selon la revendication 12, dans lequel ladite couche d'alumine est formée par chauffage de la couche d'aluminure de diffusion à une température supérieure à 982,2°C (1800°F) sous une pression partielle d'oxygène inférieure à  $1,33 \cdot 10^{-4}$  Pa ( $10^{-6}$  torr).

55. 17. Procédé selon la revendication 12, dans lequel ladite couche de barrière thermique céramique est déposée par condensation de vapeur sur ledit substrat de façon à avoir une microstructure colonnaire.

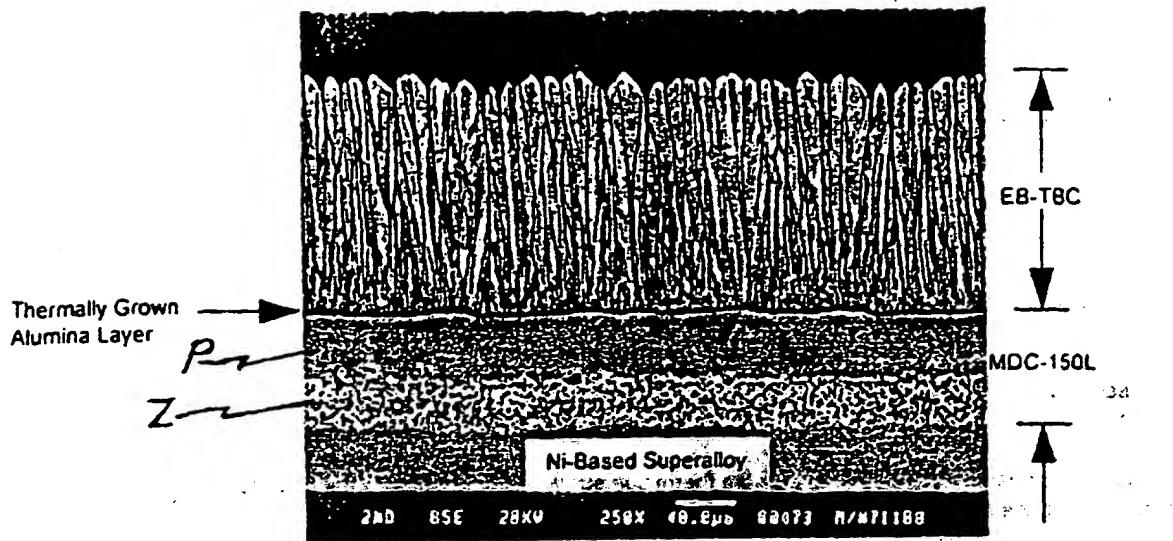


Figure 1

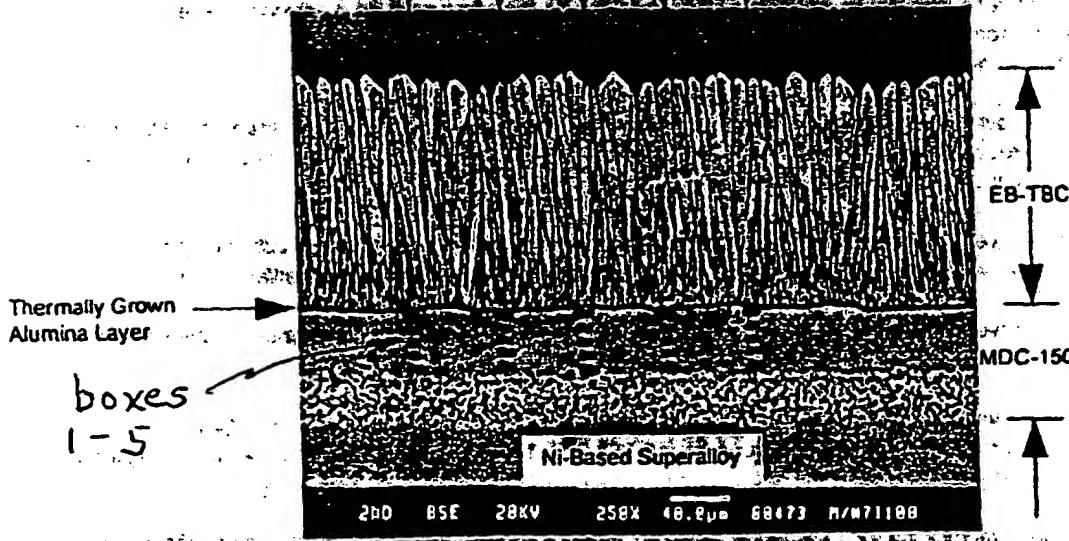


Figure 3

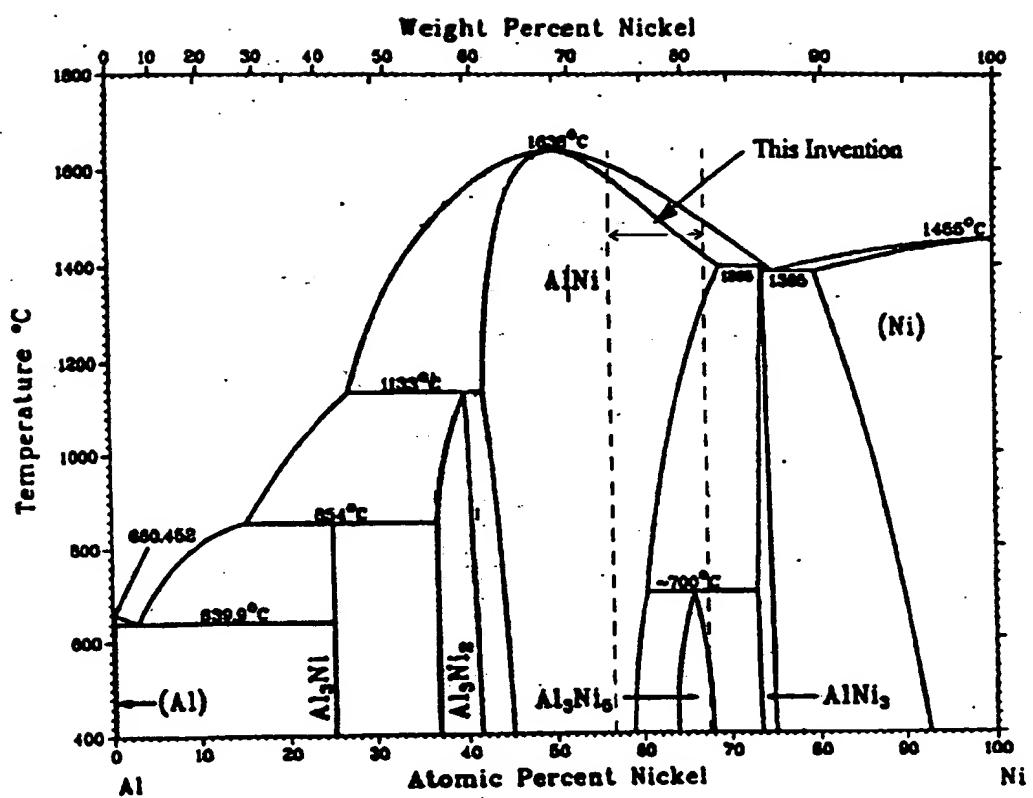
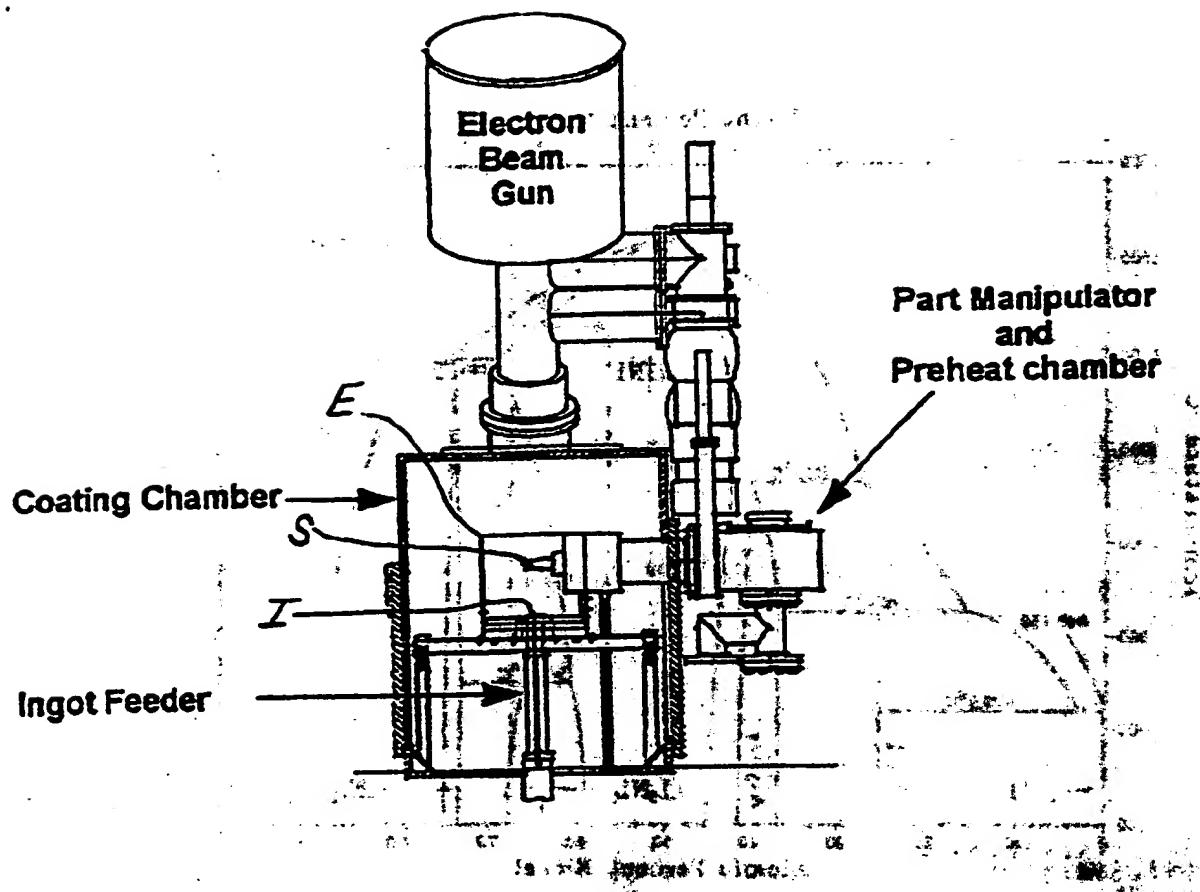


Figure 2: Ni-Al Phase Diagram



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Figure 4